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Synthesis and characterizations of quality PbS quantum dots in SBR matrix

N Dutta*, D Mohanta and A Choudhury

Department of Physics, Tezpur University PO Napaam
Sonitpur Assam-784 028 India

E-mail nabanita@tezu ernet in

Abstract We have successfully grown PbS quantum dots in styrene butadiene rubber (SBR) matrix following solution chemistry The formation of monodisperse isolated PbS quantum dots with size distribution 5–10 nm was confirmed by transmission electron micrographs Structural and optical properties have been characterized by X-ray diffractometer and photoluminescence spectroscopy Since there is significant enhancement in the band gap of quantum dots by (7-8 times 2 15 eV) compared to bulk PbS (0 29 eV at 300 K), PbS quantum dots can be promising candidates for application in optoelectronic sensors/devices operated over broad spectrum of light

Keywords PbS quantum dot, SBR latex, Photoluminescence XRD and TEM

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1 Introduction

Over the years, research in low dimensional semiconductor quantum structures, namely quantum dots have received significant attention due to size dependent electronic properties [1] Worthwhile progress has been achieved in the areas of synthesis, and characterizations *e g* investigating electrical and optical properties of quantum dots [2] These fundamental properties of nanoscaled semiconductor structures are strongly influenced by their size and dimensionality [3]. Such dependence popularly known as 'quantum size effect' offers the possibility to manipulate their properties by size and shape control Controlled variation of nanocrytallites size results in remarkable changes in the optoelectronic properties from molecular to the bulk [4, 5]. Quantum confinement effects are particularly important if the crystallite dimension is less than a critical size known as the exciton Bohr radius of the material [6].

Corresponding Author

PbS is an attractive IV–VI binary semiconductor compound having direct and narrow energy gap 0.29 eV at 300 K. It has a large bulk Bohr exciton radius (a_B ~ 18 nm), small carrier effective masses (m^* = 0 1 m_c) and large optical dielectric constant (ε = 17 2) Accordingly, strong quantum confinement effects can be easily noticed and the ground state absorption edge would be tunable over a wide range of wavelengths (from near infra red to visible). This is because the PbS quantum dots exhibit discrete electronic states distributed over a wide energy gap with respect to their narrow band gap bulk counter part [7,8].

Quantum dots embedded in polymeric matrix provide an interesting way of studying nanomaterials. Polymers are considered as good host materials capable of protecting nanoparticles from agglomeration [9, 10]. They normally offer long term stability and durability against environmental degradation. In this paper, we report the synthesis of PbS quantum dots in a flexible and nontoxic matrix namely, styrene butadiene rubber (SBR). Prepared quantum dots are characterized by X-ray diffraction (XRD), and transmission electron microscopy (TEM). In addition, effort was made to obtain distinct excitonic peaks through photoluminescence spectroscopy (PL).

2. Experimental details

The carboxylated SBR latex (99% pure, Synthomer, Germany) was selected as matrix to encapsulate the PbS uantum dots. SBR is a synthetic rubber co-polymer of butadiene and styrene (Figure 1). It is made by the freeradical polymerization in an emulsion system using redox initiators such as hydrogen peroxide and ferrous sulfate We have decided to specifically work in this medium as it provides a flexible polymer system which exhibits cistrans geometric isomers and hence capable of accommodating nanoparticles with better size dispersity.

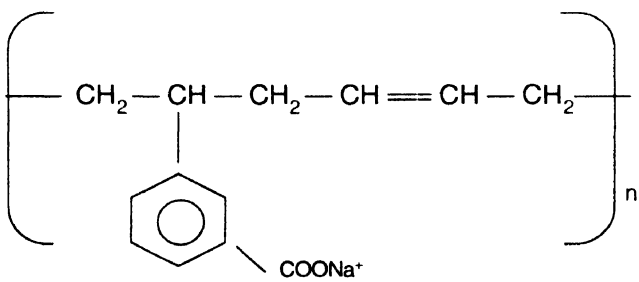

Figure 1. Structural representation of SBR copolymer

One coat of SBR latex was drawn over glass substrate and left for drying up to 24 hrs. Next, as received SBR thick films were washed in double distilled water and dipped into 0.1 M $PbCl_2$ solution up to 1 hour. Finally, the films containing Pb^{++} were treated with H_2S (prepared by Na_2S sol^n in an acidic medium). Thus, PbS quantum dots are grown in flexible SBR latex matrix. The size and distribution of the quantum dots were determined by 'TEM'. XRD was performed to obtain the information regarding its structure, crystallinity and approximate size (Model : Seifert 3003TT). PL studies has been performed as it

provides information relating to different energy states available between valence band and conduction band responsible for radiative recombination and indicates luminescence efficiency of PbS quantum dots (Amnico Brown fluorescence spectrometer).

3. Results and discussion

The TEM micrographs, shown in Figure 2(a) indicate formation of Pbs quantum dots with average size 5-10 nm. They are spherical in size and isolated from each other. The reasonable amount of inhomogeneity seen in the size distribution could be due to nonuniform incorporation of Pb^{++} into SBR coatings. The advantage is unclusteredness thus providing a system to study individual quantum dots, whcih otherwise would be difficult in nanostructured films where grain boundary effect is a serious problem [11]

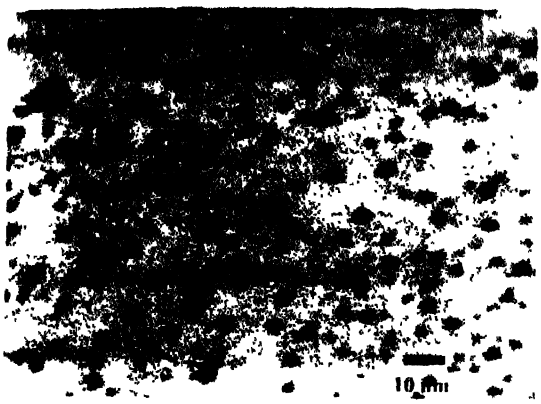

Figure 2(a). TEM micrograph of PbS quantum dots

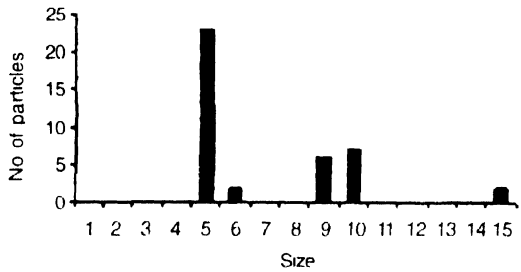

Figure 2(b). Size distribution *vs* no of PbS quantum dots

Referring to Figure 3 shows a typical X-ray diffraction Pattern of PbS quantum dots embedded in flexible SBR matrix. The XRD pattern contains Bragg's diffraction peaks corresponding to reflection from (111), (200) and (220) planes of PbS cubic rock salt structure [12, 13]. The diffraction peak signal corresponds to weak intensity owing to low concentration of PbS. The average diameter has been estimated from the line width of the

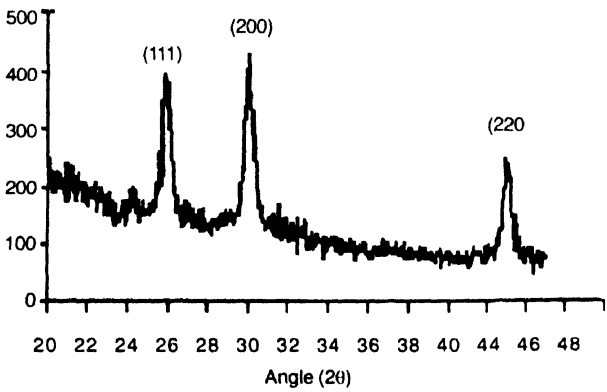

Figure 3. XRD spectra of PbS quantum dots

diffraction peaks using Scherrer formula ($D = 0.9\,\lambda/\beta\cos\varphi$), where λ is wavelength of X-ray, β is full width at half maxima and φ is the Bragg angle) found to be 9.16 nm [14]

The PL study of the PbS sample reveals three emission peaks corresponding to 573 nm and 617 nm and 825 nm respectively. The peak at 573 nm is attributed to the band edge emission of the PbS uantum dots The second peak is the excitonic peak observable at 617 nm Normally, for other binary semiconductor systems (*e.g* CdS) excitonic emission is rarely observable as it is very close to the band edge emission with energy spacing of the order of a few meV only

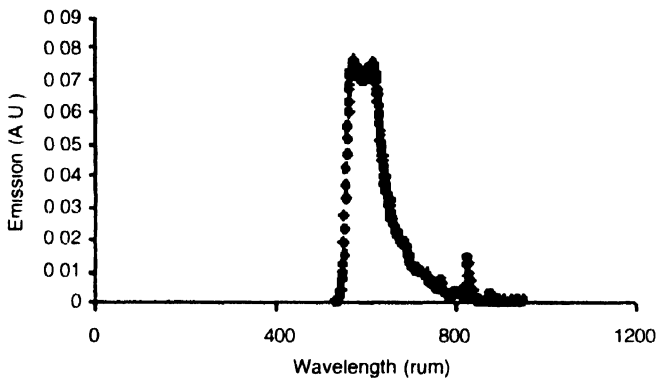

Figure 4. PL spectra of PbS quantum dots

On the other hand, in PbS system, upto ~ 10 fold energy gap enhancement might provide an opportunity to notice visible excitonic emission In our case, band edge emission (λ = 573 nm, E = 2.171 eV) and exxciton emission (λ = 617 nm, E = 2.016 eV) are well separated by an energy spacing 155 meV, which is the binding energy of our PbS quantum dots. The result of the calculation of excitonic energy in consistency with earlier reports [15]. Here the exciton energy is 2eV. Although effective mass approximation (EMA) is not valid reasonably in case of PbS [16], however since E_b is less than 100 meV, then the combination of small effective mass and large dielectric constant makes the EMA useful in case of bulk PbS [17] so using the formulae $E_b = R_y m^*/\varepsilon^2$, the exciton binding energy (E_b) for PbS bulk system has been calculated [where R_y is the Rydberg energy m^* is effective mass of electron and ε is the high frequency dielectric constant] to be 0 014 eV. Inour PbS quantum dot system, E_b (0.155 eV) has been increased by over 10 fld due to significantly large energy gap more than 10 times due to the huge energy gap enhancement (from 0.29 eV to 2.15 eV) while undergoing transition from bulk to molecular system. The third peak was visible at 825 nm, due to surface state led recombination emission. Envelope function calculationof the electronic structure of PbS uantum dots also provides the energy spectrum as well as gives selection rules for different transitions in uantum dots of smaller diameters [18]. Such calculations indicate that better emissive

property of PbS quantum dots is assured by the number of excitons staying at higher energy states However, the highest energy state of the excitons is the band edge But for better emissive properties one requires maximum numbers of excitons staying at higher energy states [19]. Combination of strong quantum confinement and high dielectric constant of PbS quantum dot system enables observation of such distinct excitonic emission peaks related to higher energy states [20]. Thus, the PL spectra obtained by us is successful in isolating such emission peaks from the band edge emission

4 Conclusion

Quality PbS quantum dots have been prepared using a very simple and less expensive process The quantum dots have been properly characterized by various techniques The possibility of obtaining stable excitons is indicated by PL spectra It may be explored further as to its origin and tunability over a given spectrum for applications in diffeent optoelectronic devices.

Increase in available number of excitons in Pbs quantum dot system brings the promise of population inversion leading to the realization of quantum dot laser Further, PbS uantum dots can be explored for generating emission extended to IR region, which would find potential in making detctors operated at IR and telecommunication wavelength

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